United States Patent [19]

Rigterink et al.

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[45] **Date of Patent: Aug. 20, 1985**

[54] **SUBSTITUTED N-AROYL N'-PHENYL UREA COMPOUNDS**

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[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **520,033**

[22] Filed: **Aug. 3, 1983**

Related U.S. Application Data

[62] Division of Ser. No. 401,491, Jul. 26, 1982, Pat. No. 4,468,405.

[51] **Int. Cl.**[3] **C07C 157/09**; C07C 122/00; C07C 127/19

[52] **U.S. Cl.** ..... **260/453 AR**; 260/454; 260/453 A; 564/26; 564/52; 564/442; 564/443; 564/440; 564/28; 564/29; 564/48; 564/49; 564/53; 564/54

[58] **Field of Search** ..... 260/454, 453 AR, 453 A; 564/26, 52, 442, 443, 440, 28, 29, 48, 49, 53, 54

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,284,628 8/1981 Nakagawa et al. 260/454

Primary Examiner—Henry R. Jiles

Assistant Examiner—Robert C. Whittenbaugh

[57] **ABSTRACT**

Dihalo and haloalkyl, haloalkoxy or haloalkylthio-substituted anilines and aniline derivatives, e.g. isocyanates that are useful in the preparation of acyl ureas having insecticidal activity.

5 Claims, No Drawings

SUBSTITUTED N-AROYL N'-PHENYL UREA COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATION

This is a divisional of application Ser. No. 401,491 filed July 26, 1982, now U.S. Pat. No. 4,468,405.

BACKGROUND OF THE INVENTION

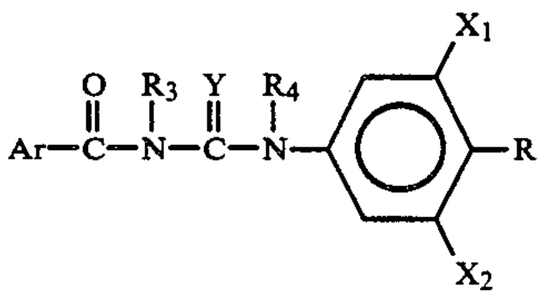
This invention relates to novel substituted N-aroyl N'-phenyl ureas, a process for producing them, insecticidal compositions containing them and a method for controlling certain insects.

Various insecticidal derivatives of urea are known in the art, such as, for example, U.S. Pat. Nos. 4,173,638; 4,005,223; 4,170,657; 4,139,636; 4,089,975 and German Patent Application No. 3,003,113.

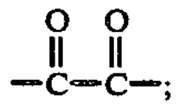
The N-aroyl N'-phenyl ureas of the present invention are more active and have a broader spectrum of effectiveness than the benzoylurea insecticides currently available.

SUMMARY OF THE INVENTION

The novel compounds of this invention are N-aroyl N'-phenyl ureas having the formula



wherein Ar is a substituted phenyl, pyridyl or pyrimidinyl radical wherein the substituents are chloro, bromo, fluoro, C_1–C_3 alkyl or C_1–C_3 alkoxy, with the proviso that at least one substituent is positioned ortho to the carbonyl group; R_3 and R_4 are individually H or C_1–C_4 alkyl or together they form the group



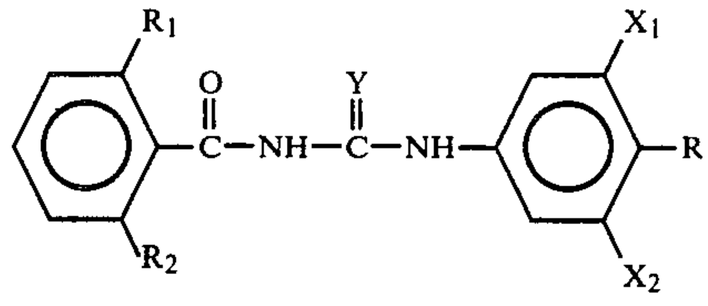
Y is O or S; X_1 and X_2 are halogen, and R is a C_1–C_4 haloalkyl, haloalkoxy or haloalkylthio group.

These novel compounds can be prepared by methods analogous to those known in the art, e.g., as taught in U.S. Pat. No. 4,139,636.

The invention also provides insecticidal compositions comprising an insecticidally effective amount of the above described N-aroyl N'-phenyl ureas in admixture with a suitable carrier or adjuvant therefore and a method for killing and/or controlling insects which comprises applying the active compound, alone or in admixture with a carrier, to the insects, the insect larvae or their habitats.

DETAILED DESCRIPTION OF THE INVENTION

The preferred compounds of this invention are those having the formula



where R_1 is F or Cl; R_2 is F, Cl or H; Y is O or S; X_1 and X_2 are halogen and R is OCF_3, OCF_2CHF_2, OCF_2CHClF, OCF_2CFHBr or OCF_2CHCl_2. Most preferably, R_1 is F or Cl R_2 is F, X_1 and X_2 *are chlorine and R is* OCF_2CHClF, OCF_2CHF_2 or OCF_2CHFBr.

The compounds of the present invention are normally crystalline solids of low solubility in water and of moderate solubility in many organic solvents. The compounds have low phytotoxicity and have exceptional activity in the control of various undesirable agricultural, household and veterinary insect pests.

Representative of the various insects which can be controlled by the active compounds of the present invention are members of the orders Lepidoptera, Coleoptera, Diptera, Orthoptera, Homoptera, Thysanoptera and Acarina. They are active against normally sensitive and resistant species at some stages of development. Examples of insect pests comprising the above include the tobacco budworm (*Heliothis virescens*), the beet armyworm (*Spodoptera exigua*), the Egyptian cotton leafworm (*Spodoptera littoralis*), the American bollworm (*Heliothis armigera*), the diamond-back moth (*Plutella maculipennis*), the gypsy moth (*Lymantria dispar*), the cutworm (*Agrotis segetum*), the Mediteranean flour moth (*Ephestia kuehniella*), the Colorado potato beetle (*Leptinotarsa decimlineata*), the mustard beetle (*Phaedon cochleariae*), the cottom boll weevil (*Anthonomus grandis*), the Mexican bean bettle (*Epilachna varivestis*), the khapra beetle (*Trogoderma granarium*), the housefly (*Musca domestica*), the lesser housefly (*Fannia canicularis*), the Mediterranean fruit fly (*Ceratitis capitata*), the black blow fly (*Phormia regina*), the cabbage rootfly (*Hylemya brassicae*), the yellow fever mosquito (*Aedes aegypti*), the malaria mosquito (*Anopheles stephensi*), the desert locust (*Schistocerca gregaria*), the migratory locust (*Locusta migratoria*), the German cockroach (*Blattells germanica*), the American cockroach (*Periplaneta americana*), the pear psylla (*Psylla pyricola*), the onion thrips (*Thrips tabaci*), and the citrus rust mite (*Phyllocoptruta oleivora*).

The compounds are highly active and can be employed to kill insects outright and/or to prevent adult emergence from juvenile forms of the insect. In such applications, the insect to be controlled and/or its habitat is contacted or treated with an insecticidal amount of one or more of the compounds of the present invention. The compounds may be administered orally to warm blooded animals from which they are excreted unchanged and they effectively combat the larvae of certain feces inhabiting insects, e.g., the face fly, horn fly and buffalo fly.

For all such uses, these compounds can be employed in unmodified form. However, the present invention embraces the use of an insecticidally-effective amount of the active ingredients in composition form with a material known in the art as an adjuvant or carrier.

Thus, for example, compositions employing one or a combination of these active ingredients can be in the form of a liquid or a dust; and the adjuvant employed

can be any one of a plurality of materials including aromatic solvents, petroleum distillates, water or other liquid carriers, propellant substances, surface-active dispersing agents, light absorbers and finely-divided carrier solids.

The exact concentration of one or a combination of the compounds of the present invention in a composition thereof with an adjuvant therefore can vary; it is only necessary that one or a combination of the compounds be present in a sufficient amount so as to make possible the application of an insecticidally-effective or inactivating dosage.

Generally, for practical applications, one or a combination of these active ingredients can be broadly applied to the insect larvae or their habitat in compositions containing from about 0.0001 to about 98 percent by weight, preferably 5 to 50 percent by weight, of the compounds.

The invention is further illustrated by the following examples.

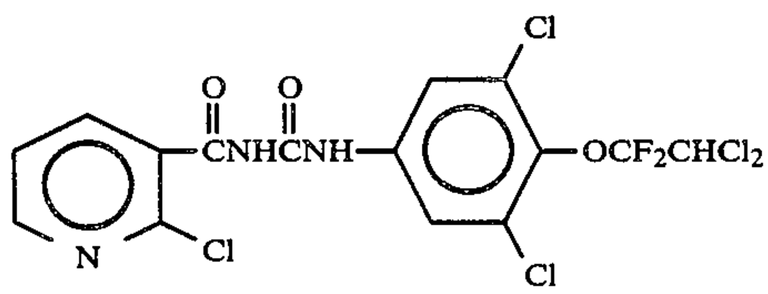
EXAMPLE 1

3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)phenyl isocynate

3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)benzenamine (12 g, 0.04 mole) was added to a solution of 20 g oxalyl chloride in 100 ml CCl_4 and heated under reflux with stirring for 0.5 hour. A solid precipitated. The carbon tetrachloride and excess oxalyl chloride were removed by evaporation in a rotary evaporator. The residue (16 g) was a slightly oily white solid, which was used in the next reaction without purification.

EXAMPLE 2

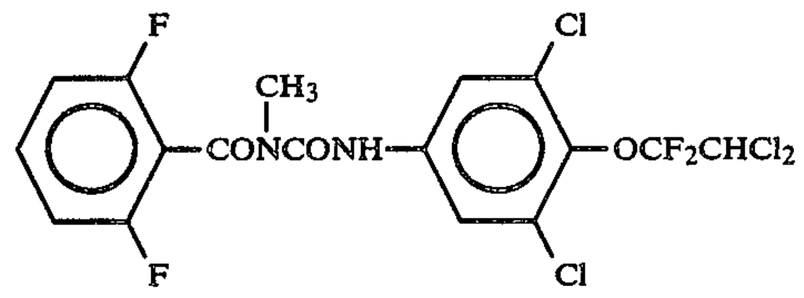
N-(((3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl)amino)carbonyl)-2-chloro-3-pyridinecarboxamide



2-Chloro-3-pyridinecarboxamide (6.3 g, 0.04 mole) and 3,5-dichloro-4-(2,2-dichloro-1,1-dichloroethoxy)-phenyl isocyanate (crude; 16 g, 0.04 mole) were added to 250 ml xylene and heated under reflux with stirring for two hours. After cooling in ice water, the precipitated product was removed by suction filtration. This was recovered as 2-chloro-3-pyridine carboxamide. A second crop was obtained by adding about 400 ml hexane to the filtrate. The second crop was a mixture of the desired material and recovered amide. The desired material was isolated and purified by recrystallizing twice from toluene. M.P.=189°–192° C. NMR spectral features supported the structural assignment.

EXAMPLE 3

N-(((3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl)amino)carbonyl)-2,6-difluoro-N-methylbenzamide

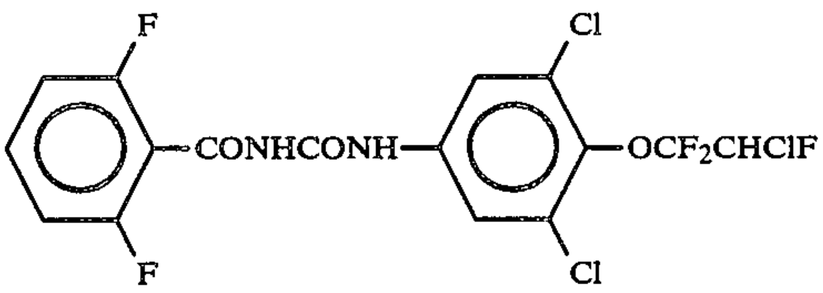


N-(((3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl)amino)carbonyl)-2,6-difluorobenzamide (9.9 g, 0.02 mole) and KOH (1.4 g, 87 percent purity, 0.02 mole) were added to 50 ml dimethylformamide with stirring, giving a clear solution. Iodomethane (3.2 g, 0.022 mole) was added and the resulting solution was stirred at room temperature for about 24 hours. The precipitated product was collected by suction filtration and dried. The product was purified by recrystallization from isopropanol. The purified product was a white solid melting at 153°–155° C. NMR spectral features support the structural assignment.

Elemental Analysis: Calcd: C, 40.18; H, 1.98; N, 5.51. Found: C, 40.3; H, 2.10; N, 5.43.

EXAMPLE 4

N-(((3,5-Dichloro-4-(2-chloro-1,1,2-trifluoroethoxy)-phenyl)amino)carbonyl)-2,6-difluorobenzamide

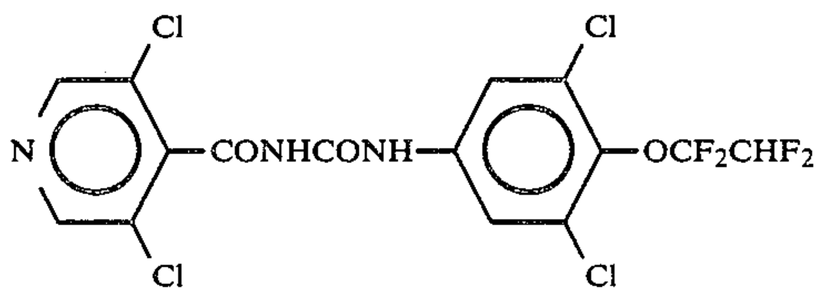


2,6-Difluorobenzoyl isocyanate (5.5 g, 0.03 mole) was added to a solution of 3,5-dichloro-4-(2-chloro-1,1,2-trifluoroethoxy)benzenamine (8.8 g, 0.03 mole) in 150 ml toluene and heated under reflux with stirring for one hour giving a clear solution. Toluene was removed by evaporation in a rotary evaporator. The residue was recrystallized from aqueous acetic acid and then from acetonitrile giving a white solid (8.3 g, 58 percent yield), melting at 178°–180° C.

Elemental analysis: Calcd: C, 40.23; H, 1.69; N, 5.87. Found: C, 40.20; H, 1.79; N, 5.83.

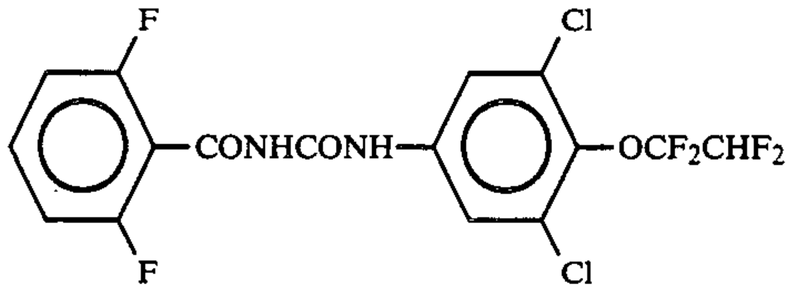
Employing the above procedures and appropriate starting materials, the following compounds were prepared:

N-(((3,5-Dichloro-4-(1,1,2,2-tetrafluoroethoxy)-phenyl)amino)carbonyl)-3,5-dichloro-4-pyridinecarboxamide.



M.P.=217°–219° C.

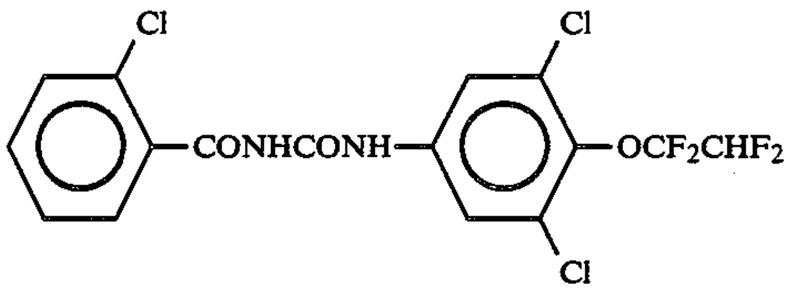
N-(((3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl-)amino)carbonyl)-2,6-difluorobenzamide.



M.P.=197°–199° C.

Analysis: Calcd: C, 41.67; H, 1.75; N, 6.08. Found: C, 41.8; H, 1.92; N, 6.06.

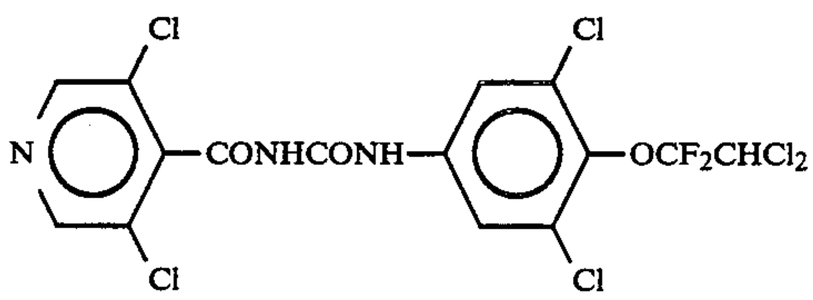
N-(((3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl-)amine)carbonyl)-2-chlorobenzamide.



M.P.=173°–175° C.

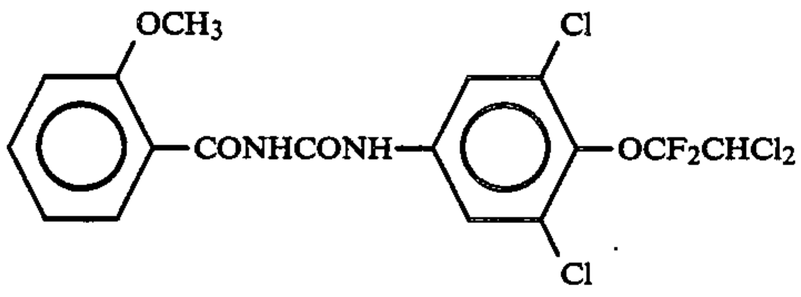
Analysis: Calcd: N, 6.10. Found: N, 6.34.

3,5-Dichloro-N-(((3,5-dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)phenyl)amino)carbonyl)-4-pyridinecarboxamide.



M.P.=228°–230° C.

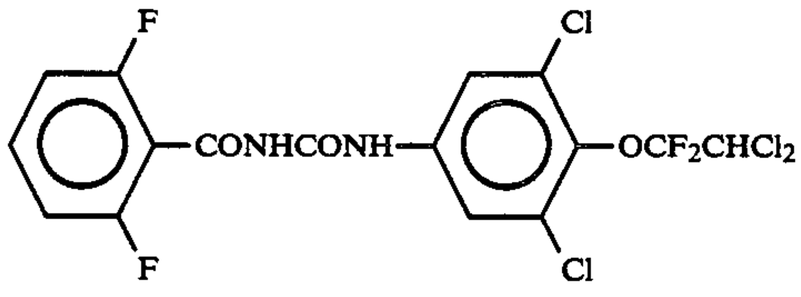
N-(((3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl)amino)carbonyl)-2-methoxybenzamide.



M.P.=156°–158° C.

Analysis: Calcd: 41.83% C; 2.48% H; 5.74% N. Found: 41.9% C; 2.57% H; 5.92% N.

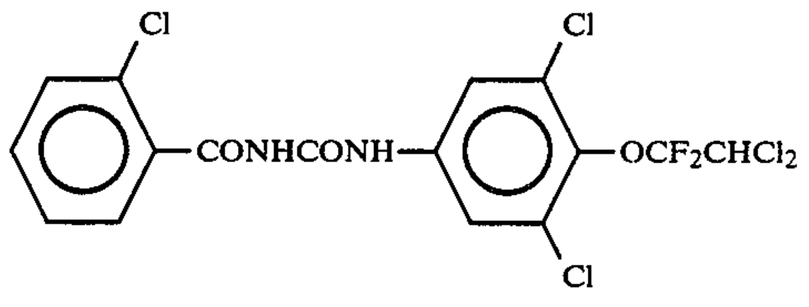
N-(((3,5-Dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl)amino)carboxyl)-2,6-difluorobenzamide.



M.P.=199°–201° C.

Analysis: Calcd: N, 5,67. Found: N, 5.66.

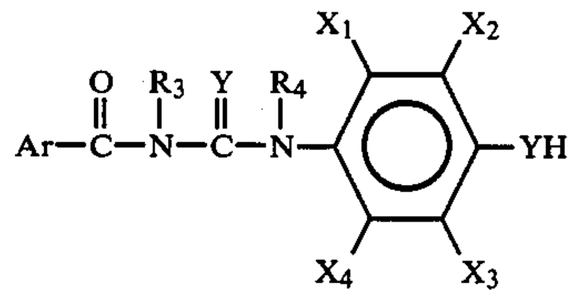
2-Chloro-N-(((3,5-dichloro-4-(2,2-dichloro-1,1-difluoroethoxy)phenyl)amino)carbonyl)benzamide.



M.P.=200°–202° C.

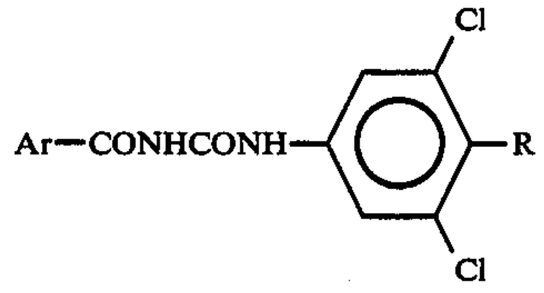
Analysis: **Calcd:** N, 5.69. Found: N, 5.60.

In addition to the above described preparative methods, many of the compounds of this invention can be made by reacting a compound having the formula



wherein all of the substituents are as above defined, with a haloalkene as is known in the art.

The biological activity of several of these compounds was determined. In the beet armyworm test, cotton leaves were dipped in aqueous suspensions of the chemicals, dried, excised and placed into petri dishes with five second-instar beet armyworm (*Spodoptera exigua*) larvae. Mortality counts were made five days later. The tobacco budworm test was the same except that five tobacco budworm (*Heliothis virescens*) larvae were placed onto the treated leaves. The results are summarized below:



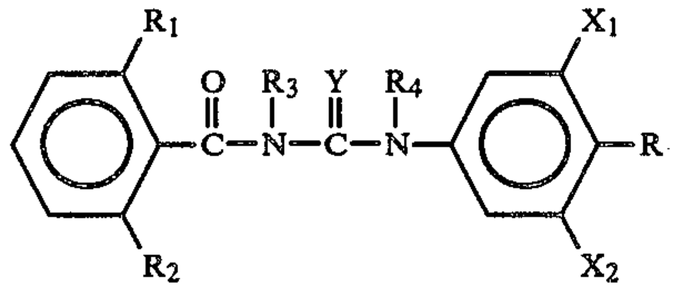
Compound	Ar	R
A	2,6-difluorophenyl	OCF_2CHCl_2
B	2-chlorophenyl	OCF_2CHCl_2

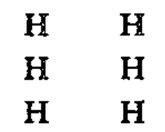
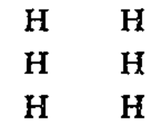
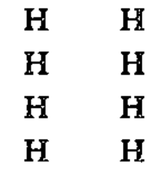
	Percent Control at Indicated Dosage, ppm					
	Beet Army Worm Test (1)			Tobacco Budworm Test (2)		
Compound	400	100	25	400	100	25
A	100	100	100	100	100	80
B	100	100	100	100	80	40

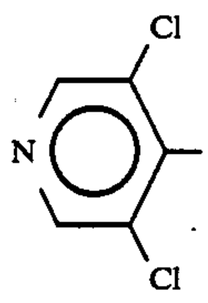
(1) Untreated check mortality 0%.

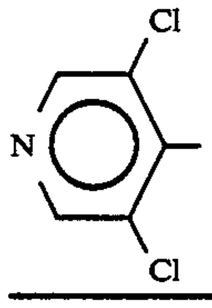
(2) Untreated check mortality 27%.

Employing the above described preparative and testing methods, the compounds listed in the following table were prepared and tested. The test results, LD_{90} ppm, indicate the dosage necessary to obtain 90 percent kill of the indicated insect.



Ex. No.	R_1	R_2	R_3	R_4	Y	X_1	X_2	R	Melting Point °C.	LD_{90}, ppm Beet Army-worm	LD_{90}, ppm Tobacco Budworm
1	F	F	H	H	O	Cl	Cl	OCF_2CHF_2	204–206	1.6	1.6
2	F	F	H	H	O	Cl	Cl	OCF_2CHFCl	176–178	1.2	1.2
3	F	F	H	H	O	Cl	Cl	OCF_2CHFBr	170–172	1.2	2.5
4	F	F	H	H	O	Cl	Cl	OCF_2CHFI	170–172		12.5
5	F	F	H	H	O	Cl	Cl	OCF_2CHCl_2	180–182	5.0	25.0
6	F	F	H	H	O	Cl	Cl	OCF_2CH_2Cl	188–190	100.0	100.0
7	F	F	H	H	O	Cl	Cl	OCF_2CHBr_2	215–217	25.0	400.0
8	F	F	H	H	O	Cl	Cl	$OCFClCHFCl$	203–205	1.25	25.0
9	F	F	H	H	O	Cl	Cl	OCF_3	218–220	0.6	12.5
10	F	F	H	H	O	Cl	Cl	OCF_2CF_3	224–227	12.5	50.0
11	F	F	H	H	O	Cl	Cl	SCF_2CHFCl	250–260	200.0	>400.0
12	F	F	H	H	O	Cl	Cl	SCF_2CHF_2	166–168	3.1	12.5
13	Cl	H	H	H	O	Cl	Cl	OCF_2CHFCl	178–180	5.0	6.2
14	Cl	H	H	H	O	Cl	Cl	OCF_2CHF_2	173–175	100.0	25.0
15	Cl	H	H	H	O	Cl	Cl	OCF_2CHFBr	183–185	2.5	10.0
16	Cl	H	H	H	O	Cl	Cl	OCF_2CHFI	171–174		50.0
17	Cl	H	H	H	O	Cl	Cl	OCF_2CHCl_2	162–164	6.2	200.0
18	Cl	H	H	H	O	Cl	Cl	OCF_2CHBr_2	217–219	25.0	400.0
19	Cl	H	H	H	O	Cl	Cl	OCF_3	203–205	2.5	12.5
20	Cl	H	H	H	S	Cl	Cl	OCF_2CHFCl	137–139	10.0	200.0
21	Cl	H	H	H	S	Cl	Cl	OCF_2CHF_2	140–142	400.0	50.0
22	F	F	H	H	S	Cl	Cl	OCF_2CHFCl	149–151	12.5	12.5
23	F	F	H	H	S	Cl	Cl	OCF_2CHF_2			
24	F	H	H	H	O	Cl	Cl	SCF_2CHFCl	245–250	>400.0	>400.0
25	F	H	H	H	O	Cl	Cl	OCF_2CHFCl	165–167	100.0	25.0
26	F	Cl	H	H	O	Cl	Cl	OCF_2CHF_2			
27	F	Cl	H	H	O	Cl	Cl	OCF_2CHFCl	205–207	2.5	5.0
28	F	Cl	H	H	O	Cl	Cl	OCF_2CHFBr	184–186	2.5	5.0
29	Cl	Cl	H	H	O	Cl	Cl	OCF_2CHF_2	217–219	25.0	25.0
30	Cl	Cl	H	H	O	Cl	Cl	OCF_2CHFCl	221–223	6.2	25.0
31	Cl	Cl	H	H	O	Cl	Cl	OCF_2CHFBr	200–202	100.0	12.5
32	Cl	Cl	H	H	O	Cl	Cl	SCF_2CHF_2	213–215	50.0	200.0
33	F	F	CH_3	H	O	Cl	Cl	OCF_2CHCl_2	153–155	100.0	>400.0
34	F	F	CH_3	H	O	Cl	Cl	OCF_2CHFCl	128–130	100.0	50.0
35	F	F	CH_3	H	O	Cl	Cl	OCF_2CHF_2	102–104	100.0	50.0
36	F	F			O	Cl	Cl	OCF_2CHCl_2	194–197	400.0	>400.0
37	F	F			O	Cl	Cl	OCF_2CHF_2	166–169	100.0	>400.0
38	F	F			O	Cl	Cl	OCF_2CHFCl	190–192	400.0	400.0
39	F	F	H	H	O	Br	Br	OCF_2CHF_2	201–203	3.7	10.0
40	CH_3	H	H	H	O	Cl	Cl	OCF_2CHFCl	163–165		>200.0
41	CH_3	CH_3	H	H	O	Cl	Cl	OCF_2CHFCl	175–177		200.0
42	C_2H_5	C_2H_5	H	H	O	Cl	Cl	OCF_2CHFCl	182–184	100.0	400.0
43	OCH_3	H	H	H	O	Cl	Cl	OCF_2CHCl_2	156–158	>400.0	>400.0
44	OCH_3	OCH_3	H	H	O	Cl	Cl	OCF_2CHFCl	203–206	100.0	25.0
45	$OCH(CH_3)_2$	H	H	H	O	Cl	Cl	OCF_2CHFCl	239–241	>400.0	>400.0
46	$OCH(CH_3)_2$	H	H	H	O	Cl	Cl	OCF_2CHF_2	242–244	>400.0	>400.0





Ar	R	M.P., °C.	LD_{90}, ppm Beet Armyworm	LD_{90}, ppm Tobacco Budworm
	OCF_2CHCl_2	189–192	100	>400
	OCF_2CHF_2	217–219	>400	>400
	OCF_2CHCl_2	228–230	>400	>400

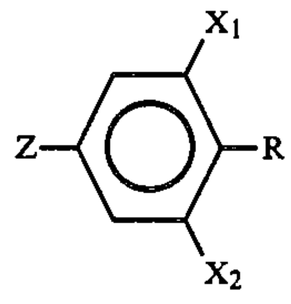
In further embodiments, the compounds of the present invention or compositions containing the same, can be advantageously employed in combination with one or more additional pesticidal compounds. Such additional pesticidal compounds may be insecticides, nematocides, acaricides, herbicides, fungicides or bactericides that are compatible with the compounds of the present invention in the medium selected for application and not antagonistic to the activity of the present compounds. Accordingly, in such embodiments the pesticidal compound is employed as a supplemental toxicant for the same or for a different pesticidal use, or as an additament. The compounds in combination can generally be present in the ratio of from 1 to 100 parts of the compound of the present invention with from 100 to 1 parts of the additional compound(s).

The compounds of this invention are, or tend to be, slow acting, i.e., they disrupt the molting of the insect, thereby killing it. As a result, some time can pass before the insects are killed. Accordingly, an increased benefit can be obtained by combining the compounds of this invention with quicker acting insecticides such as, for example organophosphorus compounds, carbamates and pyrethroids. Because of this different mode of action, the compounds of this invention kill or control insects which have, or may be developing, resistance to the more common insecticides and thus they inhibit or delay the development of resistance to such insecticides.

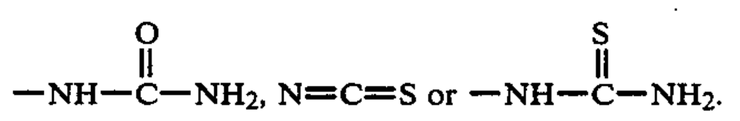
Various modifications may be made in the present invention without departing from the spirit or scope thereof and it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A compound having the formula



wherein X_1 and X_2 are halogen which may be the same or different, R is a C_1–C_4 haloloweralkyl, haloloweralkoxy or haloloweralkylthio group and Z is NH_2, —N=C=O,



2. Compound of claim **1** wherein X_1 and X_2 are independently F, Cl or Br and R is OCF_3, OCF_2CHCl_2, OCF_2CHF_2, OCF_2CHFCl or OCF_2CHFBr.

3. Compound of claim **2** wherein X_1 and X_2 are both Cl and R is OCF_2CHF_2.

4. Compound of claim **2** wherein X_1 and X_2 are both Cl and R is OCF_2CHFCl.

5. Compound of claim **2** wherein X_1 and X_2 are both Cl and R is OCF_2CHFBr.

* * * * *

REEXAMINATION CERTIFICATE (905th)

United States Patent [19]

Rigterink et al.

[11] **B1 4,536,341**

[45] Certificate Issued **Jul. 26, 1988**

[54] **SUBSTITUTED N-AROYL N-PHENYL UREA COMPOUNDS**

[75] Inventors: **Raymond H. Rigterink**, Midland, Mich.; **Ronald J. Sbragia**, Clayton, Calif.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

Reexamination Request:
No. 90/001,143, Dec. 22, 1986

Reexamination Certificate for:

Patent No.:	**4,536,341**
Issued:	**Aug. 20, 1985**
Appl. No.:	**520,033**
Filed:	**Aug. 3, 1983**

Related U.S. Application Data

[62] Division of Ser. No. 401,491, Jul. 26, 1982, Pat. No. 4,468,405.

[51] **Int. Cl.**[4] **C07C 119/048**; C07C 127/22; C07C 153/057; C07C 157/12

[52] **U.S. Cl.** **558/13**; 560/358; 564/23; 564/26; 564/28; 564/29; 564/44; 564/48; 564/49; 564/52; 564/53; 564/54; 564/440; 564/442; 564/443

[58] **Field of Search** 560/358; 558/13; 564/23, 26, 28, 29, 44, 48, 49, 53, 52, 54, 440, 442, 443

[56] **References Cited**

FOREIGN PATENT DOCUMENTS

762485 7/1967 Canada 564/442

Primary Examiner—Alan Rotman

[57] **ABSTRACT**

Dihalo and haloalkyl, haloalkoxy or haloalkylthio-substituted anilines and aniline derivatives, e.g. isocyanates that are useful in the preparation of acyl ureas having insecticidal activity.

REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307

THE PATENT IS HEREBY AMENDED AS INDICATED BELOW.

Matter enclosed in heavy brackets [ ] appeared in the patent, but has been deleted and is no longer a part of the patent; matter printed in italics indicates additions made to the patent.

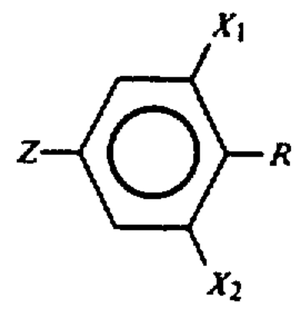
AS A RESULT OF REEXAMINATION, IT HAS BEEN DETERMINED THAT:

Claim **1** is cancelled.

Claim **2** is determined to be patentable as amended.

Claims **3–5**, dependent on an amended claim, are determined to be patentable.

2. [Compound of claim 1] *A compound having the formula*



wherein X_1 and X_2 are independently F, Cl or Br, [and] R is OCF_3, OCF_2CHCl_2, OCF_2CHF_2, OCF_2CHFCl or OCF_2CHFBr *and Z is* NH_2, $-N=C=O$, $-NH-\overset{O}{\overset{\|}{C}}-NH_2$, $-N=C=S$ *or* $-NH-\overset{S}{\overset{\|}{C}}-NH_2$.

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